AU-A-17506/88

88-158456/23 A88 J01 L02 NIGO- 22.04.85
JAPAN GOATEX KK *J6 3099-246-A
00.00.87-JP-240627 (+JP-084590) *(30.04.88)* B01d-13/04 C08j-09/42

Electrolytic diaphragm membrane material - comprises porous PTFE film with fluoro ion exchange resin
C88-070860

A(4-E8A, 4-E10, 12-E9, 12-S6C1, 12-W11A, 12-W11L) J(1-C3, 1-E3E, 1-H, 3-B3A, 4-B1) NO L CODES

A membranous material comprises a porous film of PTFE with 3-90wt.% of perfluoro-type ion-exchange resin uniformly attached and integrated. The porous film of PTFE is either sufficiently impregnated with a soln. of perfluoro-type ion-exchange resin to obtain a tight membranous material or insufficiently impregnated with the soln. to obtain a porous membranous material.

In ann. to these, the membranous material can be obtd. by (e.g., mixing PTFE with a soln. of ion-exchange resin and forming the resulting mixt. into a film or forming the ion-exchange resin into a film and laminating it on the porous film of PTFE). The membranous material is (e.g., 3-50 microns thick). The porous film of PTFE has pore content of (e.g., at least 40%).

USE/ADVANTAGE - The membranous material is used for electrolytic diaphragm, sepg. membranes for gases and liqs., filters, and enzyme-immobilising membranes. It has excellent mechanical strength and dimensional stability. (4pp Dwg.No.0/0)

BEST AVAILABLE COPY

(12) PATENT ABSTRACT (11) Document No. AU-A-17506/88
(19) AUSTRALIAN PATENT OFFICE

(54) Title
A COMPOSITE FILM MATERIAL

(51)4 International Patent Classification
B32B 027/08 C08J 005/22

(21) Application No. : 17506/88 (22) Application Date : 08.06.88

(30) Priority Data

(31) Number (32) Date (33) Country
62-240627 28.09.87 JP JAPAN

(43) Publication Date : 6.4.89

(71) Applicant
JAPAN GORE-TEX, INC.

(72) Inventor
NAME NOT GIVEN

(74) Attorney or Agent
GRIFFITH HACK & CO. MELBOURNE

(57) Claim

1. A composite film material comprising a perfluoro-type ion exchange resin combined with a film of porous, expanded polytetrafluoroethylene to form a uniform integral unit, wherein the weight ratio of perfluoro-type ion exchange resin relative to said porous, expanded polytetrafluoroethylene is 3% to 90% based upon the weight of the composite.

AUSTRALIA

PATENTS ACT 1952

Form 10

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number:
Lodged:

Complete Specification-Lodged:
Accepted:
Lapsed:
Published:

Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant: JAPAN GORE-TEX,INC.

Address of Applicant: 42-5,1-CHOME,AKAZUTSUMI
SETAGAYA-KU,
TOKYO 156
JAPAN

Actual Inventor:

Address for Service: CLEMENT HACK & CO.,
601 St. Kilda Road,
Melbourne, Victoria 3004,
Australia.

Complete Specification for the invention entitled:
A COMPOSITE FILM MATERIAL

The following statement is a full description of this invention including the best method of performing it known to me:-

BACKGROUND OF THE INVENTION

The present invention relates to a composite film material. An object of the present invention is to provide a functional composite film material which is suitable for the treatment of various types of liquids and gases, for example, for the separation or other functional treatment of various types of liquids or gases, or for degassing or gas infusion, etc.

Various types of synthetic resin films have been employed for the purpose of separating various types of liquids and gases, subjecting such liquids and gases to other functional treatments and achieving degassing or gas diffusion and infusion. For example, ion exchange resins in the form of natural, microporous macromolecular films such as cellophane and films formed by graft-polymerizing acrylic acid or methacrylic acid with plastic films, have been used as separators in batteries. Porous resin films have been used to diffuse gases into liquids and to degas liquids. Porous resin films have also been used in various types of filters.

Resin films with various separating functions have been utilized in order to separate specified components from various types of mixed liquids or mixed gases.

However, there have been numerous problems associated with the conventional films described above. For example, when films formed from ion exchange resins are made into thin films, or when the exchange capacity is increased, there are resulting problems associated with decreased strength and decreased stability in liquids. Films made of natural, microporous macromolecular films suffer from a serious tendency to deteriorate as a result of oxidation by oxidizers. Furthermore, films formed by graft-polymerizing acrylic

acid with a plastic film suffer from problems in terms of diffusion of the active substance and corrosion. In addition, such resin films are generally water-repellent and have various effects on fine gas particles. Accordingly, such films cannot sufficiently achieve the objective of fine, uniform gas diffusion with high efficiency.

In cases where hydrophobic porous resin films are used as filters in aqueous systems, various problems can arise, e.g., a high osmotic pressure must be applied, etc. Moreover, heat-resistant separating films which have a high selective permeability to water are extremely limited.

SUMMARY OF THE INVENTION

A composite film material is provided comprising a perfluoro-type ion exchange resin combined with a film of porous, expanded polytetrafluoroethylene to form a uniform integral unit, wherein the weight ratio of perfluoro-type ion exchange resin relative to the porous, expanded polytetrafluoroethylene is 3% to 90% based upon the weight of the composite. The ion exchange resin may be bonded to the porous, expanded polytetrafluoroethylene as a thin film thereon or the ion exchange resin may be impregnated into the pores of the porous, expanded polytetrafluoroethylene. The impregnated composite film may be substantially porous or substantially nonporous. Preferably, the weight ratio in the composite is 10% to 30%.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

A composite film material is provided in which a perfluoro-type ion exchange resin is combined with a film of porous, expanded polytetrafluoroethylene to form a uniform integral unit, wherein the weight ratio of perfluoro-type ion exchange resin relative to the porous polytetrafluoroethylene is 3% to 90% based upon the weight of the composite. The perfluoro-type ion exchange resin may be bonded to the porous polytetrafluoroethylene as a thin film or, preferably, the ion exchange resin may be impregnated into the porous polytetrafluoroethylene film. The composite film may be porous or it may be substantially solid, depending on the loading of ion exchange resin. The composite is useful for the separation or other functional treatment of various types of liquids and gases.

Specifically, the present invention is a composite material which is characterized by the fact that a perfluoro-type ion exchange resin is combined with a porous, expanded polytetrafluoroethylene film to form a uniform, integral unit at a weight ratio of 3% to 90% perfluoro-type ion exchange resin relative to the porous polytetrafluoroethylene film.

Methods for making porous, expanded polytetrafluoroethylene are disclosed in U.S. Patent 3,953,566. That reference also discloses methods of bonding other polymer films to porous, expanded polytetrafluoroethylene and impregnating other polymers into porous, expanded polytetrafluoroethylene. There is no mention in the reference of ion exchange resins of any type.

Porous, expanded polytetrafluoroethylene film is water-repellent and has high mechanical strength and dimensional stability in liquid. By using such a porous, expanded polytetrafluoroethylene film as a substrate, it is possible to form the aforementioned perfluoro-type ion exchange resin film as a thin film bonded to the polytetrafluoroethylene. Preferably, the ion exchange resin film can be stably formed by impregnation and invasion of and bonding within the porous structure of the porous polytetrafluoroethylene. The perfluoro-type ion exchange resin film has hydrophilic properties. By forming such a hydrophilic thin film on the water-repellent polytetrafluoroethylene film, it is possible to alter the characteristics of the composite film with respect to liquids. Specifically, in the case of a solid composite film, the film will be selectively permeable to components such as water, which have an affinity for the aforementioned perfluoro-type ion exchange resin. Furthermore, in the case of a continuously porous composite film whose pore surfaces are uniformly covered by a perfluoro-type ion exchange resin, the osmotic pressure will decrease as a result of the change in the pore surface characteristics, so that the passage of water is facilitated. Such a film will have improved usefulness as a filter for use in aqueous systems. Furthermore, in the case of a film used for gas diffusion in an aqueous system, the gas diffusion obtained using a composite film whose pore surfaces are covered with a perfluoro-type ion exchange resin is far finer, more uniform and more efficient than gas diffusion obtained using a film whose pore surfaces are not covered with a perfluoro-type ion exchange resin. Moreover, a porous, expanded polytetrafluoroethylene film alone has no functional groups and is therefore not usually suitable for chemical treatments.

However, a perfluoro-type ion exchange resin has functional groups. Accordingly, by making a composite of a polytetrafluoroethylene film and a perfluoro-type ion exchange resin, it is possible to realize various types of chemical functions utilizing functional groups such as enzyme fixation.

The abovementioned change in characteristics with respect to liquids can be achieved by setting the content of the aforementioned perfluoro-type ion exchange resin at 3% or greater relative to the amount of porous, expanded polytetrafluoroethylene film used. By setting this amount at 90% or less, it is possible to obtain mechanical strength and dimensional stability using the aforementioned porous polytetrafluoroethylene film as a substrate.

According to the invention, a composite film is formed by combining a perfluoro-type ion exchange resin with a porous, expanded polytetrafluoroethylene film having a porosity of 35% or greater, preferably 40% or greater, so that an integral, uniform composite body is formed. This combination into an integral composite can be accomplished either by fusing a perfluoro-type ion exchange resin to the polytetrafluoroethylene film or by coating the polytetrafluoroethylene film with a liquid coating of a perfluoro-type ion exchange resin, or by immersing the polytetrafluoroethylene film in a solution of a perfluoro-type ion exchange resin. According to the invention, all available perfluoro-type ion exchange resins are suitable if they can be provided in the form of a solution. Some typical methods for achieving such an integral bonding of a polytetrafluoroethylene film and a perfluoro-type ion exchange resin are set forth below. Any of these methods may be used.

(1) Formation of a solid film by thoroughly impregnating a porous, expanded polytetrafluoroethylene film with a perfluoro-type ion exchange resin solution.

(2) Formation of a porous composite film by partially impregnating the aforementioned porous, expanded polytetrafluoroethylene film with a perfluoro-type ion exchange resin solution in method (1) above.

(3) Formation of a solid composite film by mixing an ion exchange resin solution with a porous, expanded polytetrafluoroethylene resin.

(4) Formation of a porous film by stretching or drawing the composite film formed by method (3) above.

(5) Forming an ion exchange resin into a thin film, and then laminating this with a porous, expanded polytetrafluoroethylene film.

In all of the above cases, the weight ratio of perfluoro-type ion exchange resin to porous, expanded polytetrafluoroethylene should be in the range of 3% to 90%, and a weight ratio of 10% to 30% is especially desirable. Furthermore, the overall film thickness is generally 1 to 300 microns, and preferably is 3 to 50 microns.

The thickness of the porous, expanded polytetrafluoroethylene film is generally about 1 to 300 microns, and preferably is 3 to 50 microns.

The film-form material obtained as described above can be used for various purposes in treating liquids and gases. For example, this material may be used to remove gas components from liquids, to add gases to liquids, or to form functional films such as electrolysis diaphragms, gas or liquid separating membranes, especially membranes which are selectively permeable to water, filters or chemical-reaction-promoting films such as enzyme-fixing films.

This material is a thin film material with desirable mechanical strength and dimensional stability and can be used to obtain numerous superior functions which cannot be obtained using porous, expanded polytetrafluoroethylene films alone.

In cases where this material is used for separators in halogen-zinc batteries, the separators thus obtained have superior mechanical strength and dimensional stability as described above. Furthermore, these separators are not generally susceptible to electrolyte-caused deterioration, and they have low electrical resistance and superior coulomb efficiency. The useful life of the resulting battery itself is also long.

The porosity of the porous, expanded polytetrafluoroethylene films used in accordance with the invention is between about 40% and about 90% and the average pore size is preferably between 0.1 and 10 microns.

As stated above, every perfluoro-type ion exchange resin can be used if it can be obtained in the form of a solution. An example is a copolymer of tetrafluoroethylene with perfluorovinylether containing a carboxylic acid group or a sulfonic acid group in the side chain. This can be placed in the form of a solution using acetone or ethanol as the solvent, preferably in a concentration range between 5% and 15%, by weight, of resin, based upon the weight of the solution.

One method to prepare a composite of the invention is to fix a film of porous, expanded polytetrafluoroethylene at four sides in a frame to prevent any dimensional change. The film is then coated with the abovementioned ion exchange resin solution or entirely immersed in the solution. This process may be repeated several times. The resin fills the pores of the porous, expanded

polytetrafluoroethylene film. After impregnation, the film is heated at a temperature between 100°C and 200°C for a sufficient time to evaporate the solvent. The ion exchange group in the impregnated resin may be converted in advance into a heat-resistant group such as an ester group or a metal salt group, and then the film may be heated above the melting point of porous, expanded polytetrafluoroethylene followed by returning the above-converted ion exchange group to the original acid group. The composite film thus obtained is solid.

A porous, expanded polytetrafluoroethylene film may be fixed at the circumference and then immersed in a 5% to 10% ion exchange resin solution as above. The solution is uniformly and sufficiently impregnated into the film pores preferably by means such as applying supersonic waves. Then the solvent is evaporated so that the ion exchange resin adheres uniformly to the internal surfaces of the pores of the porous, expanded polytetrafluoroethylene film, leaving the composite film in a porous state. The film thus obtained is then stabilized by heating in the same manner as above.

According to the invention, the product for use in enzyme-fixing is manufactured such that the porous, expanded polytetrafluoroethylene film is incorporated with the perfluoro-type ion exchange resin and the enzyme is then fixed to it. In this case, the fixing strength is sufficiently high and the loaded quantity of the enzyme is sufficiently high because of the high porosity of the porous, expanded polytetrafluoroethylene film. Furthermore, the enzyme is ionicly bonded to the ion exchange resin layer of the film, so the bonding is easily carried out in a mild condition without decreasing the enzyme activity.

In addition, the product has a characteristic that the enzyme has difficulty in detaching because it is fixed to the internal surface of the minute pores of the film.

As described above, the present invention makes it possible to obtain a composite film material which is superior in terms of mechanical strength and dimensional stability, which can be made hydrophilic overall or simultaneously water-repellent and hydrophilic according to the conditions of manufacture, and which has desirable characteristics for utilization in various types of equipment for treating liquids and gases, such as separating membranes or reaction membranes. Thus, the present invention has great industrial value.

While the invention has been disclosed herein in connection with certain embodiments and detailed descriptions, it will be clear to one skilled in the art that modifications or variations of such details can be made without deviating from the gist of this invention, and such modifications or variations are considered to be within the scope of the claims hereinbelow.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A composite film material comprising a perfluoro-type ion exchange resin combined with a film of porous, expanded polytetrafluoroethylene to form a uniform integral unit, wherein the weight ratio of perfluoro-type ion exchange resin relative to said porous, expanded polytetrafluoroethylene is 3% to 90% based upon the weight of the composite.

2. The composite film of claim 1 wherein said ion exchange resin is bonded to said porous, expanded polytetrafluoroethylene as a thin film thereon.

3. The composite film of claim 1 wherein said ion exchange resin is impregnated into the pores of said porous, expanded polytetrafluoroethylene.

4. The composite film of claim 3 which is substantially porous.

5. The composite film of claim 3 which is substantially nonporous.

6. The composite film of claim 1 wherein said weight ratio is 10% to 30%.

DATED THIS 8TH DAY OF JUNE 1988
JAPAN GORE-TEX, INC.
By its Patent Attorneys:
CLEMENT HACK & CO.
Fellows Institute of Patent
Attorneys of Australia

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☑ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.